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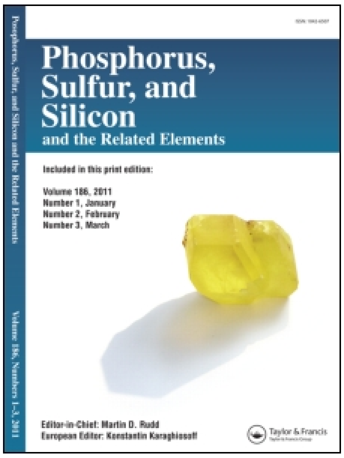

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
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STUDIES ON 2-MERCAPTOCOUMARINOXAZOLE SYSTEMS: SYNTHESIS OF NOVEL TYPES OF 2-MERCAPTO-8-METHYL-6H-PYRANO-(3,2-f)BENZOXAZOLE-6-ONE DERIVATIVES—Part-II

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To cite this Article Rao, B. Rajeshwar , Mouli, G. V. P. Chandra and Reddy, Y. D.(1982) 'STUDIES ON 2-MERCAPTOCOUMARINOXAZOLE SYSTEMS: SYNTHESIS OF NOVEL TYPES OF 2-MERCAPTO-8-METHYL-6H-PYRANO-(3,2-f)BENZOXAZOLE-6-ONE DERIVATIVES—Part-II', Phosphorus, Sulfur, and Silicon and the Related Elements, 14: 1, 37 — 40

To link to this Article: DOI: 10.1080/03086648208073108

URL: http://dx.doi.org/10.1080/03086648208073108

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Phosphorus and Sulfur, 1982, Vol. 14, pp. 37–40
0308-664X/82/1401-0037/$06.50/0

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STUDIES ON 2-MERCAPTOCOUMARINOXAZOLE SYSTEMS: SYNTHESIS OF NOVEL TYPES OF 2-MERCAPTO-8-METHYL-6H-PYRANO-(3,2-f)BENZOXAZOLE-6-ONE DERIVATIVES—Part-II

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(*Received June 2, 1982*)

6-Amino-7-hydroxy-4-methylcoumarins (Ia and Ib) are treated with carbondisulphide in alkaline medium to furnish the novel and hitherto unknown 2-mercapto-8-methyl-6H-pyrano(3,2-f)benzoxazoles (IIa and IIIa). Treatment of IIa and IIIa with alkyl halides and acid halides gives the corresponding thioethers II (b–g) and III (b–g) and thioesters II (h–j) and III (h–j) respectively. These are characterized on the basis of their elemental analyses, IR, PMR and mass spectral data.

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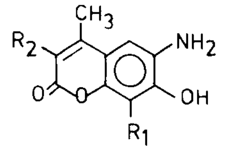
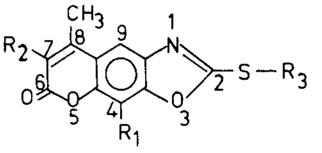
2-Mercaptonaphthoxazoles[1] have been shown to exhibit remarkable antibacterial and antifungal activities. 6-Pyrazolo- 6-isoxazolo and pyrano-benzoxazoles have a wide spectrum of biological activity.[2,3] Induced by these observations, we wish to report here the preparation of the hitherto unknown 2-mercapto-8-methyl-6H-pyrano(3,2-f) benzoxazole-6-one derivatives with a view to evaluating their antibacterial and antifungal activities.

6-Amino-7-hydroxy-4-methyl-3-phenylcoumarin (Ia) and 6-amino-7-hydroxy-4,8-dimethylcoumarin (Ib) were treated with carbondisulphide in the presence of aqueous methanolic potassium hydroxide to furnish 2-mercapto-8-methyl-7-phenyl-6H-pyrano(3,2-f)benzoxazole-6-one (IIa) and 2-mercapto-4,8-dimethyl-6H-pyrano(3,2-f)benzoxazole-6-one (IIIa), respectively. The structures assigned to (IIa and IIIa) were established on the basis of elemental analysis and IR spectra as detailed below.



I
a : $R_1=H$; $R_2=C_6H_5$
b : $R_1=CH_3$; $R_2=H$



IIa : $R_1=R_3=H$; $R_2=C_6H_5$
IIb-j : $R_1=H$; $R_2=C_6H_5$; R_3=alkyl/acyl
IIIa : $R_1=CH_3$; $R_2=R_3=H$
IIIb-j : $R_1=CH_3$; $R_2=H$; R_3=alkyl/acyl

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TABLE I

Physical data of 2-mercapto-8-methyl-6H-pyrano(3,2-f)benzoxazole-6-one derivatives. (II and III)

Compound[a]	R_3	mp[b] °C	Mol. formula	Found (Calc.)%	
				N	S
		$R_1 = H$; $R_2 = C_6H_5$			
IIa	$—H$	270	$C_{17}H_{11}NO_3S$	4.51 (4.53)	10.32 (10.35)
IIb	$—CH_3$	225	$C_{18}H_{13}NO_3S$	4.31 (4.33)	9.82 (9.9)
IIc	$—CH_2—CH_3$	191	$C_{19}H_{15}NO_3S$	4.0 (4.15)	9.3 (9.49)
IId	$—(CH_2)_2—CH_3$	188	$C_{20}H_{17}NO_3S$	3.8 (3.98)	9.02 (9.11)
IIe	$—(CH_2)_3—CH_3$	179	$C_{21}H_{19}NO_3S$	3.53 (3.83)	8.53 (8.76)
IIf	$—CH_2—CH{=}CH_2$	295	$C_{20}H_{15}NO_3S$	4.0 (4.01)	8.9 (9.16)
IIg	$—CH_2—C_6H_5$	196	$C_{24}H_{17}NO_3S$	3.4 (3.5)	8.0 (8.02)
IIh	$—CO—CH_3$	297	$C_{19}H_{13}NO_4S$	3.78 (3.98)	9.0 (9.11)
IIi	$—CO—C_6H_5$	290	$C_{24}H_{15}NO_4S$	3.26 (3.38)	7.56 (7.74)
IIj	$—CO—CH{=}CH—C_6H_5$	>300	$C_{26}H_{17}NO_4S$	3.01 (3.19)	7.12 (7.28)
		$R_1 = CH_3$; $R_2 = H$			
IIIa	$—H$	290	$C_{12}H_9NO_3S$	5.43 (5.66)	12.78 (12.95)
IIIb	$—CH_3$	187	$C_{13}H_{11}NO_3S$	5.28 (5.36)	12.13 (12.26)
IIIc	$—CH_2—CH_3$	151	$C_{14}H_{13}NO_3S$	5.0 (5.09)	11.52 (11.63)
IIId	$—(CH_2)_2—CH_3$	142	$C_{15}H_{15}NO_3S$	4.72 (4.84)	11.0 (11.07)
IIIe	$—(CH_2)_3—CH_3$	155	$C_{16}H_{17}NO_3S$	4.41 (4.62)	10.43 (10.56)
IIIf	$—CH_2—CH{=}CH_2$	271	$C_{15}H_{13}NO_3S$	4.73 (4.87)	11.03 (11.15)
IIIg	$—CH_2—C_6H_5$	158	$C_{19}H_{15}NO_3S$	4.03 (4.15)	9.32 (9.49)
IIIh	$—CO—CH_3$	>300	$C_{14}H_{11}NO_4S$	4.75 (4.84)	10.87 (11.07)
IIIi	$—CO—C_6H_5$	295	$C_{19}H_{13}NO_4S$	3.74 (3.98)	8.97 (9.11)
IIIj	$—CO—CH{=}CH—C_6H_5$	>300	$C_{21}H_{15}NO_4S$	3.53 (3.71)	8.37 (8.48)

[a] Compounds were obtained in 60–70% yields, and satisfactory C and H analysis have been obtained for all the compounds.

[b] Compounds IIf,g,j, IIIc,f,g,h, were crystallized from dioxane-water, the rest were crystallized from ethanol-water.

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The products IIa and IIIa indicated absorption bands at 1520–1510 cm^{-1} (N—C=S), 1070–1060 cm^{-1} (C=S).[4] The bands at 1650 cm^{-1}, 1590 cm^{-1}, 1360 cm^{-1} and 1180 cm^{-1} were assigned to the vibrations arising from the heterocyclic oxazole system,[5] which were totally absent in the IR spectra of their precursors i.e. (Ia and Ib). All these compounds (Ia, Ib, IIa and IIIa) indicated, as expected, the absorption band at 1730–1700 cm^{-1} characteristic of the lactonic carbonyl group.

Treatment of IIa and IIIa with alkyl halides and acid halides in the presence of methanolic potassium hydroxide gave the corresponding thioethers II (b–g) and III (b–g) and thioesters II (h–j) and III (h–j) respectively (Table I).

The IR spectra of II (b–j) and III (b–j) revealed the absence of the band corresponding to the C=S group. However, in each case, strong absorption bands appeared at 1730–1700 cm^{-1} (lactone, $>$C=O) and 1640 cm^{-1}, 1590 cm^{-1}, 1360 cm^{-1} and 1180 cm^{-1} were in agreement with the heterocyclic oxazole ring system.

The mass spectrum of IIg showed peaks at m/z 399 (M^+) (22.88%), 366 (M-SH) (3.18%), 280 (2.09%), 166 (1.42%), 165 (2.82%), 115 (1.5%), 92 (7.29%), 91 (100%), 77 (1.69%), 69 (2.11%), 65 (4.34%). The ratio of intensity of the isotropic peaks $(M + 1)^+$ and $(M + 2)^+$ with the parent peak indicates the presence of one sulfur atom. The base peak at m/z 91 is attributable to the tropylium cation.

The PMR spectrum of IIg in $CDCl_3$ (chemical shifts in δ-ppm down field from TMS internal reference) exhibited singlets at δ2.2 (3H, —CH_3), δ4.4 (2H, —S—CH_2—Ph), and δ7.7 (1H, C_4). The C_9 proton along with other aromatic protons appeared as a multiplet at δ7.0–7.5 (11H).

The biological studies on the compounds are under investigation and the results will be published later.

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EXPERIMENTAL

Melting points were determined in open capillaries using sulphuric acid bath and are uncorrected. IR spectra (ν_{max} in cm^{-1}) were recorded in KBr disc and nujol mull on a Perkin-Elmer 283 instrument, 90 MHz PMR spectrum in $CDCl_3$ was recorded on a Varian Spectrometer using TMS as internal standard (chemical shifts in δ-ppm) and mass spectrum on a JMS-D300 (JAPAN) mass spectrometer at 70 eV.

Preparation of 2-Mercapto-8-methyl-6H-pyrano(3,2-f)benzoxazole-6-one (IIa and IIIa): General procedure: A mixture of the appropriate 6-amino-7-hydroxy-4-methylcoumarin (Ia and b; 0.1 mol), carbondisulphide (10ml), potassium hydroxide (0.02 ml), methyl alcohol (40 ml) and water (10 ml) was refluxed for 30 hours and cooled. On acidification a solid was thrown out. It was filtered and recrystallized from aqueous alcohol to furnish the analytical samples (IIa and IIIa) (Vide Table I).

Reaction of IIa and IIIa with alkyl halides and acid halides: General procedure: Compound IIa/IIIa (0.005 mol) was dissolved in methanol (20 ml) in the presence of potassium hydroxide (0.005 mol) and the appropriate alkyl halide (0.005 mol) or acid halide (0.005 mol) was added and refluxed for 4 hours and cooled. The compound precipitated was filtered and recrystallized from a suitable solvent to give the corresponding thioethers II (b–g) and III (b–g) and thioesters II (h–j) and III (h–j) (Table I).

ACKNOWLEDGMENT

The authors are thankful to Prof. K. Koteswara Rao, Principal, Regional Engineering College, Warangal for providing facilities and to Prof. S. R. Ramadas, Department of Chemistry, I.I.T., Madras for his invaluable suggestions. One of the authors (BRR) is thankful to CSIR, New Delhi (INDIA) for the award of a Junior Research Fellowship.

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